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URBANA

REPORT OF INVESTIGATIONS 190

SOME EXPERIMENTAL FACTORS THAT MODIFY
DIFFERENTIAL THERMOGRAMS OF BITUMINOUS COAL

BY

KENNETH E. CLEGG



PRINTED BY AUTHORITY OF THE STATE OF ILLINOIS

URBANA, ILLINOIS

1955

ILLINOIS STATE GEOLOGICAL SURVEY



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KENNETH E. CLEGG

ABSTRACT

Investigation of bituminous coal by an adaptation of differential thermal analysis in which the sample is covered and heated in the absence of free air shows that the resulting thermogram is strongly influenced by several experimental factors.

The coal undergoes thermal decomposition, and the thermogram reflects the predominantly endothermic chemical and physical reactions taking place. Peak shifting, change of peak height, variation of temperature range, and/or interruption of devolatilization occur when amounts of inert diluent in the specimen, maximum particle size, rate of temperature increase, manner of covering the specimen, manner of packing, or geometry of the specimen holder are varied.

Variation in thermograms from random samples of bright clarain selected from the same diamond drill core of coal shows the need for sampling techniques that will insure samples representative of the coal being tested.

A series of progressively altered thermogram types was obtained by manipulating one or more experimental factors. Curves fitting into this series were then produced by progressively altering one factor while keeping all others as nearly constant as possible. Any one thermogram type could be reproduced with reasonable accuracy only when all experimental factors and sampling techniques were duplicated.

The ultimate cause of variation in thermograms is shown to be related to the ease and manner in which decomposition gases escape from the sample, and to pressure developed inside the specimen well.

The studies emphasize the need of care both in adopting and maintaining constant experimental conditions and in selecting and preparing the specimen when differential thermal analysis of coal is conducted under conditions that restrain swelling of the sample and expansion and escape of volatile matter.

INTRODUCTION

ANALYSES OF COAL are essential to its well-planned use, and various physical and chemical analytic procedures are used in the laboratory. Differential thermal analysis is a relatively new method of evaluating certain characteristics of coal. This report deals with factors that affect the results of differential thermal analysis of coal.

The influence of experimental factors on differential thermograms of clay minerals has been aptly demonstrated and discussed (Arens, 1951). However, the great diversity of results obtained by various workers who have applied differential thermal analysis to coal has indicated the need of a similar study of some of these factors and their relation to coal thermograms. The tests discussed in this report were designed to fill that need in part.

These studies have a twofold purpose. First, they were designed to determine to

what extent and in what manner differential thermograms of coal are influenced by factors other than differences in the coal itself. In this respect they may be regarded as a progress report because factors other than those herein considered, and their resultant problems, require further investigation.

Second, the studies may be regarded as an initial attempt to evaluate the thermal technique as it applies to coal, and to determine what particular adaptations are most suitable for coal analysis. The great variety of results obtained by various workers shows that some methods result in thermograms with much more detail than others. It seems desirable, therefore, to determine which adaptations will yield thermograms with maximum interpretable detail and consistently good reproducibility.

The first differential thermal analysis of coal probably was made by Hollings and Cobb (1923), who heated their samples in

a nitrogen atmosphere and used coke as the reference material. Various adaptations of the technique, such as heating in oxygen, in an inert gas, in air, in partial vacuum, under pressure, or with a cover over the assay, have more recently been used (Stott and Baker, 1953; Whitehead, 1950; Whitehead and Breger, 1950; Breger, 1950; Glass, 1954; and others).

In the study reported here, oxidation was inhibited, but not completely prevented, by covering the specimen or packing it tightly in a deep sample well. The coal was thereby subjected to carbonization and distillation. Laboratory studies of coal carbonization and distillation are not new, but the use of differential temperatures is a relatively new approach to analyzing carbonization reactions.

Except for the covering of the assay, the method is similar to that applied to clays and mixtures of coal and clay minerals by Grim and Rowland (1952). The assay covering, added to adapt the method to coal, was used by Glass (1954) in a study of coal rank.

ACKNOWLEDGMENTS

G. H. Cady, Senior Geologist and Head, Emeritus, of the Coal Division of the Illinois State Geological Survey, supplied the coal used for test material in this study. He also obtained the chemical analysis and made the profile measurements of banded ingredients.

The manuscript was critically read by O. W. Rees, J. S. Machin, J. E. Lamar, J. A. Simon, A. C. Bevan, H. D. Glass, Raymond Siever, and J. A. Harrison of the Survey staff, and by C. E. Marshall, visiting research scientist from the Department of Geology and Geophysics, University of Sydney, Sydney, Australia.

EQUIPMENT AND MATERIAL

EQUIPMENT

A Stone style B variable pressure differential thermal analysis unit was used for the investigation. Minor adjustments were made so that the equipment could be used without employing pressure or controlled

atmosphere. The arrangement of the unit and recording equipment is shown in figure 1.

A spherical pressure chamber with an inside diameter of 8 inches encloses the specimen holder and heating unit. The upper half of the pressure sphere was not used.

The specimen holder used for most of the tests was a cylinder of inconel steel 11½ inches in diameter supported vertically just below the center of the pressure sphere by two stainless steel rods. Two ½-inch diameter wells for the sample and reference material are drilled 1 inch deep parallel to the length of the cylinder. A flat nickel plate 1/16 of an inch thick and large enough to cover both wells was used as a lid. The depth of the wells was adjusted by placing at the bottom one or more ceramic disks 1/10 of an inch thick. This method admittedly is not absolutely equivalent to deeper or shallower wells because the disks are pervious to gas and hence give a "cushioning" effect that would not normally be present. Also, the thermocouples were in effect brought 1/10 of an inch nearer the bottom of the wells for each disk inserted.

A few runs were made with nickel specimen holders having the same outside diameter as the inconel but with smaller wells. The results obtained with them will be discussed in relation to their thermograms.

A platinum-platinum 10% rhodium furnace temperature thermocouple is located in the reference well. A double-junction difference thermocouple, consisting of two platinum leads joined by a platinum 10% rhodium wire, has one junction in the reference well and the other in the specimen well. All thermocouple leads run to a small Dewar flask for cold junctions.

A cylindrical heating unit fits down over the sample holder. The inside is approximately 3 inches in diameter and 2¼ inches deep, with a heating element of 12 coiled kanthal wires evenly spaced about the periphery and extending vertically through its length. Two inches of refractory brick insulation surrounds the heating element. The entire assembly is covered with sheet aluminum with several turns of copper tub-

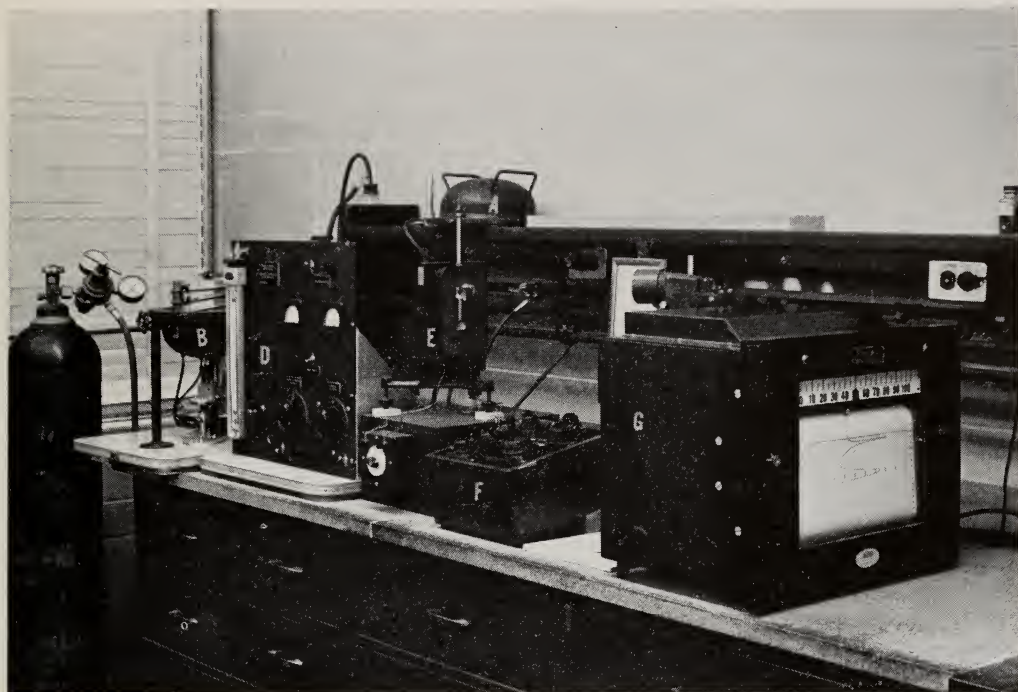


FIG. 1.—Differential thermal apparatus and recording equipment used in investigating experimental factors. A. upper half of pressure sphere; B. lower half of pressure sphere; C. heating unit, in place; D. control panel of driving mechanism; E. galvanometer; F. potentiometer; G. photopen recorder.

ing around the outside. Water flowing through the tubing keeps the outside of the unit cool. The top is closed and the base fits closely upon a stand of refractory brick which surrounds the two rods supporting the specimen holder. The arrangement is thus designed to hold convection flow of air to a minimum.

The controlling mechanism is a variable-speed motor-controlled powerstat that permits a wide range of heating rates. Furnace temperatures are read directly on a Brown portable potentiometer. Differential temperatures are reflected by a suspension mirror galvanometer, and the thermogram is recorded directly by a Beckman photopen recorder. Resistance in series with the galvanometer can be varied from zero to 300 ohms in steps of 50 ohms.

TEST MATERIAL

A quartered section of a 2-inch diameter diamond drill core of high-volatile C bright-banded bituminous coal was used as a standard test material. Its ingredient content, de-

termined by megascopic measurement of a polished surface, was: vitrain,* 18.1%; fusain, 2.56%; bright clarain, 51.1%; dull clarain, 27.7%; pyrite, 0.5%; and other mineral matter, 0.1%. Chemical analysis of the core "as received" was: moisture, 10%; volatile matter, 35.44%; fixed carbon, 42.43%; sulfur, 3.28%; ash, 12.13%; and Btu, 10,961. The Btu on a mineral-free basis is 12,688.

The core was collected at the drilling site, wrapped in heavy waxed paper, and brought directly to the laboratory. There it was split in half lengthwise, and one half was again split lengthwise. The half core was polished for measurement of banded ingredients. One of the quarter sections was prepared for chemical analysis, and the one to be used in this study was put into a container with a tight-fitting lid. To retard evaporation, a moist paper was placed in the container and, except when samples were being removed, the lid was kept in place. Ther-

*Only those bands of vitrain 1 mm. or thicker were assigned to the total vitrain content. Bands less than 1 mm. were included as a constituent of clarain.

mograms produced periodically under identical conditions throughout the 12-month period of investigation showed that any oxidation or weathering during that period was too minor to be reflected.

TECHNIQUES

SAMPLING

Sampling was first attempted by selecting narrow-banded bright clarain for each run. Variations in thermograms, however, indicated that consistently uniform specimens could not be selected by this method. To avoid this variability (believed to result from the heterogeneity of banded coal), enough bright-banded clarain was taken for all runs needed to test any one experimental factor. This was crushed and sieved to 10 by 28 mesh size and the fines discarded. The coarse fraction was kept in a screw-cap bottle from which samples were taken as required for each run and crushed to a finer size (normally to minus 100 mesh). This method assured that samples for all curves of a particular experimental factor were sufficiently uniform.

Final grinding, done immediately before each test, restored fresh particle surfaces so that the effect of any oxidation taking place during the one or two days required for all tests of one experimental factor was considered negligible. The fact that the samples were not representative of the whole coal core was of small consequence because the tests were designed to study experimental factors related to coal rather than coal itself.

PACKING

Methods of packing the specimen are designated as loose, medium, and tight. Loose packing was accomplished by pouring the material into the sample well until it was filled and a small cone, its base flush with the top, had formed. The sample holder was then tapped lightly until settling had rounded off the top of the cone at the level of the well rim. Too much tapping caused excessive settling, but with proper care reproduction of thermograms was good and considered to be well within normal

limits of accuracy for the methods and equipment used.

For medium packing, the sample well was filled as above, but tapping and refilling were continued until the material would settle no more. A steel plunger, 3 inches long and weighing about 43 grams, was then placed lightly on top of the material and immediately lifted off. Enough material was added to refill the well, and application of the plunger was repeated. This procedure was continued until the well remained full under the weight of the plunger. Of the three packing methods used, this one afforded the least accurate reproduction of thermograms.

A specimen was tightly packed by filling the well and pressing the material down as firmly as possible with the steel plunger. Filling and pressing were repeated until the well remained filled to the top. This method gave reasonably good reproducibility of thermograms.

Although most runs were made with a full well, several analyses were made with a $\frac{1}{4}$ -inch air space left between the specimen and the cover. The resulting thermograms did not differ greatly from those obtained by using a shallower specimen well (fig. 5).

PARTICLE SIZE

Except when the effect of maximum particle-size differences was tested, all analyses were made with the coal crushed to minus 100 mesh. Grinding and crushing was done with mortar and pestle, with frequent sievings made to avoid an excess of very small sizes in the assay.

GALVANOMETER RESISTANCE

A resistance of 50 ohms was used in series with the galvanometer for all except one set of tests. For those made to show the effect of variation on peak height, resistance was varied.

HEATING RATE

The standard rate of heating was about 10° C. per minute. Corrections for slight irregularities in the rate were not made when the original thermograms were re-

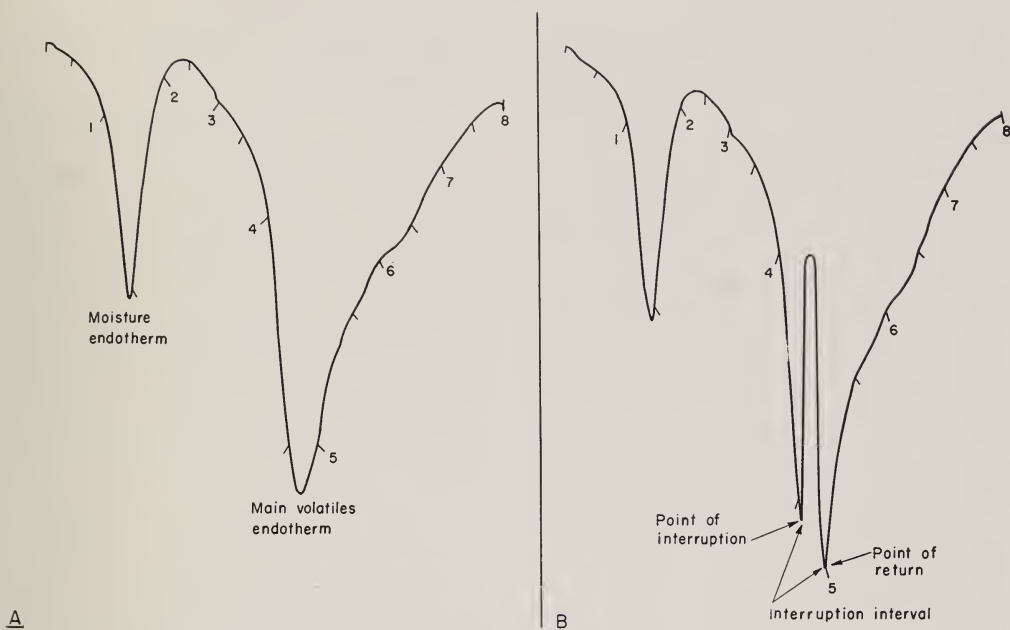


FIG. 2.—Uninterrupted (A) and interrupted (B) thermograms showing terminology used in this report.

produced for printing. The degree of irregularity may thus be observed and taken into consideration when the thermograms are studied.

REFERENCE MATERIAL

Alundum (aluminum oxide calcined to 1250° C.) was used as the inert reference material and also as a diluent when diluted samples were analyzed.

THEORETICAL ASPECTS

TERMINOLOGY

In this report, the large endotherm that reaches its apex between 450° and 500° C. will be called the *main volatiles endotherm*. It may occur in *uninterrupted* or *interrupted* form (fig. 2). The interrupted endotherm is characterized by a *point of interruption*, an *interruption interval*, and a *point of return* (fig. 2B). Interruption intervals may vary greatly in width, i.e., horizontal dimension. A narrow interruption interval may involve a time lapse of about 5 minutes and a temperature range of about 50° C., whereas a wide interval may require from 45 to 50 minutes and an increase of 450° to 460° C. No cognizance will be taken of

the vertical dimension of the re-entrant, that being a function of peak height of the main volatiles endotherm.

A series of thermogram types consists of a number of thermograms grading from those with small uninterrupted endotherms, through those with increasing peak height to the interrupted type with narrow interruption intervals, and thence through the relatively complex types having increasingly wider intervals. Figure 7 shows two well-developed series of thermogram types. This development from simple to comparatively complex types can be obtained by varying several experimental factors, or by progressively altering only one while all others remain constant.

CONCEPTS OF COAL CARBONIZATION

Detailed consideration of the theoretical aspects of the differential thermograms is not the purpose of this report. However, recognition of the general nature of processes involved during distillation and carbonization of coal in the absence of air, or in limited air, is necessary for an understanding of why the thermograms react as they do to experimental factors.

These processes were briefly summarized

by Stutzer and Noe (1940) as: loss of water up to 100° C., evolution of CO₂ and H₂S up to about 330° C., and of CH₄, H₂, and NH₃ up to about 800° C., and release of H₂ for the most part above that temperature. Low temperature tar was referred to as "primary tar," and the process of its formation as "low temperature carbonization."

Katwinkle (*in* National Research Council, 1945, p. 172-173) observed the formation of light oil and gas after exclusion of moisture. At higher temperatures, as the coal began to soften, decomposition products were mainly brown and black primary tar. Tar evolution subsided during the softening range and, as swelling progressed, the volatiles consisted only of gas. Gas evolution was strongest in the latter part of the softening range, it decreased rapidly thereafter through resolidification, and then remained constant or rose slightly in the semicoke zone. In low-rank noncaking coals, gas evolution was greatest before softening temperatures were reached.

Sweitoslawski (1942, p. 103-105), in discussing the amount of energy absorbed during the coking process, divided the exchange into three stages corresponding to the three stages of carbonization.

In the first stage, heat is required to raise the temperature of the coal from the starting point to the softening temperature. The main quantity of heat is absorbed by evaporation of water in the coal.

In the second stage, the melting and heating of the coal to its resolidification temperature takes place. Heat is absorbed in the melting process and in thermal decomposition.

In the third stage, the transformation of semicoke into coke occurs during which, in addition to the heat required for heating the material, relatively large amounts of heat are required for some of the endothermic reactions that take place during this period. The main reactions are: (1) reduction of CO₂ to CO; (2) reduction of water with formation of H₂ and CO; and (3) decomposition of methane and other hydrocarbons, with the formation of H₂ and some unsaturated hydrocarbons. Presumably the CO₂ referred to in the first step is that re-

sulting from the presence of air in the coal charge, and the water in the second step is chemically bound water.

Sweitoslawski recognized that almost all of these later reactions are typically reversible processes that can reach a state of equilibrium under optimum conditions. However, he pointed out two factors usually present to prevent establishment of equilibriums: (1) the time is too short, and (2) the quantities of reacting gases are very small in comparison to the quantities of the solid phase. The surface of the solid phase is inhomogeneous, and therefore the gases react only with those areas that are characterized by the presence of more active atoms.

PROCESSES OCCURRING IN THE DIFFERENTIAL THERMAL FURNACE

The processes taking place in the differential thermal furnace, as adapted for this investigation, are mainly endothermic. The heating rate is too fast for the establishment of equilibriums in the reversible reactions at higher temperatures. The thermograms appear to reflect two opposing forces, endothermic and exothermic, with the exothermic tendencies shown by the minor deflections that develop upon the larger endotherms. Some of the smaller deflections within the interruption interval of the more complex thermograms may be especially likely to reflect exothermic tendencies. The wider interruption intervals are a result of the inability of early formed decomposition products to escape from the sample, leaving them available for further reactions at higher temperatures.

The solid residue left in the sample well after the heating of coal to various temperatures yields information pertinent to an understanding of the thermograms. At 300° C. no visible change in the appearance of the coal could be detected, but gas evolution was already underway and was reflected by downward sweep of the thermogram. Above 400° to 420° C., immediately prior to the point of interruption of the main volatiles endotherm, slight evidence of softening was shown by the rounding of some coal particles. Cohesion was weak and the residue crumbled under slight pressure. The top

and sides of the specimen holder were covered with a thick deposit of soot or carbon. Above 450° C., immediately following upward movement from the point of interruption, little or no further change in the coal was visibly detectable. At the point of return from a narrow interruption interval, however, the coal had reached its resolidification temperature. Cohesion of coal particles was considerably better than at 450° C. The soot deposit had begun to disappear, and at a still higher temperature had disappeared entirely. A thin film of ash usually covered part of the surface of the assay when the temperature went above 650° to 700° C. The significance of oxidation will be briefly considered later in this report.

Residue formed during heating under conditions that gave a wide interruption interval showed that vesiculation was not complete at 500° to 550° C. if endothermic downsweep to the point of return had not been completed. Better cohesion of coal particles resulted than when the interruption interval was narrow.

The residue of samples giving uninterrupted endotherms appeared to have undergone about the same degree of physical change at comparable temperatures as those of samples that produced curves with narrow interruption intervals, but cohesion of particles appeared to be somewhat weaker.

INTERPRETATION OF THERMOGRAMS

Major features of the differential thermograms shown in this report were interpreted on the basis of the above observations and those of other workers who have studied coal carbonization and distillation under many kinds of experimental conditions.

The first major endotherm is the result of loss of moisture. The temperature at which it reaches its apex reflects nonequilibrium conditions. These conditions prevail throughout the entire heating range.

Exothermic reaction is thought to follow water loss. Upward deflection of the thermogram is more pronounced when samples are loosely packed or run in comparatively shallow specimen wells. During the short interval between the end of moisture loss

and the start of volatiles escape, a small amount of air, unhindered by outflowing gas, may enter the specimen well and enhance oxidation.

The main volatiles endotherm, which usually begins to develop at around 300° C., reflects evolution of volatile matter. The size and shape of the endotherm, however, is controlled not only by the formation of gas but also by the ease and manner of its escape from the sample. Endothermic cooling is a function of the escape of those molecules of greater thermal energy from the rest of the comparatively cooler sample. If this escape is delayed until higher temperature is reached, devolatilization proceeds at an accelerated rate and the endotherm is steeper and has greater peak height.

If, however, at or near the time of maximum gas escape, and when endothermic cooling of the sample is most pronounced, a factor suddenly stops or greatly retards the process, a condition of considerable thermal unbalance exists with no cooling process to support it. The establishment of such a condition appears to initiate interruption intervals.

Davidson (*in* National Research Council, 1945, p. 211) observed, while using an adaptation of the Foxwell apparatus, which involved heating coal in a tube through which a stream of inert nitrogen flowed, that resistance during the plastic stage was sometimes so great that it caused complete stoppage and even reversal of the nitrogen stream. The tube became choked as the softening and swelling coal and coal tars sealed the interstitial space between coal particles.

The adherence of coal particles in the specimen well of the differential thermal apparatus showed that, at the temperature of interruption of the main volatiles endotherm, primary tars and tar mists had formed a seal sufficient to stop temporarily the passage of decomposition gas through the interstices. This is believed to be the cause of temporary stoppage of gas escape at a time of considerable thermal unbalance, and of initiation of the interruption interval.

A second factor that contributes to the development of interrupted endotherms is

heat transfer through the massive sample holder. Absorbed heat tends to disperse equally throughout a medium until uniformity is attained. Coal is a good heat absorber but a poor heat conductor. The metal of the specimen holder, on the other hand, is an excellent conductor. The thermal conductivity of inconel is about .036, considerably greater than that of coal.

The effects of this difference in thermal properties are reflected by a temperature reversal at the beginning of the interruption interval. Immediately following the point of interruption of the main volatiles endotherm, and as the line is returning upwards, the temperature indicator of the potentiometer comes to a stop and then reverses its direction. On curves 159, 162, and 163 of figure 6, two ticks denoting temperatures of 450° C. have been placed. These are furnace temperatures recorded as the indicator reached 450° C., reversed temporarily, and a few moments later again advanced. A loss of as much as 15° to 20° C. has been observed, but 10° to 15° C. is more normal. This phenomenon was not observed with uninterrupted endotherms. It shows that adjacent to the furnace thermocouple in the reference material heat is being lost at a faster rate than it is being replaced by the furnace.

This temperature reversal occurs when endothermic cooling has exerted its maximum effect upon the coal sample. It is concluded, therefore, that furnace heat is flowing from the hotter areas of the specimen holder towards the comparatively cooler and highly absorptive coal. If heat is flowing from the vicinity of the furnace thermocouple in the reference material and towards the coal, it must also affect the differential thermocouples by counteracting the temperature relationship previously established by endothermic reaction.

To summarize, the interruption interval is a result of the combination of two processes: (1) sealing of interstitial particle space temporarily interrupting gas escape at a time of excessive thermal unbalance; (2) transfer of furnace heat from the area of the differential thermocouple in the reference material to the one in the sample. The

results are reflected on the thermogram by sudden stop of endothermic downsweep, immediately followed by rapid upward return as thermal balance is established between the two thermocouples. Because the heat involved is not heat of reaction, the re-entrant is not an exotherm.

The duration of the interruption and the width of the interruption interval depend upon resistance to pressure developed inside the specimen well. If the coal is one that becomes highly fluid during the plastic stage, gas pressure may soon become sufficient to induce vesiculation. Gas escape is then renewed suddenly and at an accelerated rate; the coal vesiculates and then resolidifies into semicoke. A sudden downsweep to the point of return on the thermogram reflects the process. If the furnace is opened at the time of the point of return, a vesicular residue is found in the sample well. If the coal is more viscous during plasticity, or if artificial conditions impose greater resistance to expansion, vesiculation and accompanying downsweep to the point of return proceed more slowly and are not completed until more time has elapsed and higher temperature is reached.

Complete fluidity is not necessary to cause interruption of gas escape from the specimen well. A bituminous shale, such as the Chattanooga, does not become completely plastic. However, the main volatiles endotherm can be interrupted by the formation of tars and liquid hydrocarbons and controlled by the same experimental factors that control it in a coal sample (fig. 3). A sample of cellulose, obtained by scraping the surface of filter paper, reacts the same way when the cotton-like material is packed into a deep specimen well. Unless it is tightly packed, however, an uninterrupted endotherm results.

In curves 173 and 174 (fig. 7), opposing forces (expansion and resistance thereto) are so nearly balanced that the endotherm may or may not be interrupted. Identical samples and experimental conditions were used for both curves. A similar balance has been attained by manipulation of other experimental factors, and in each case the interruption could be controlled by increas-

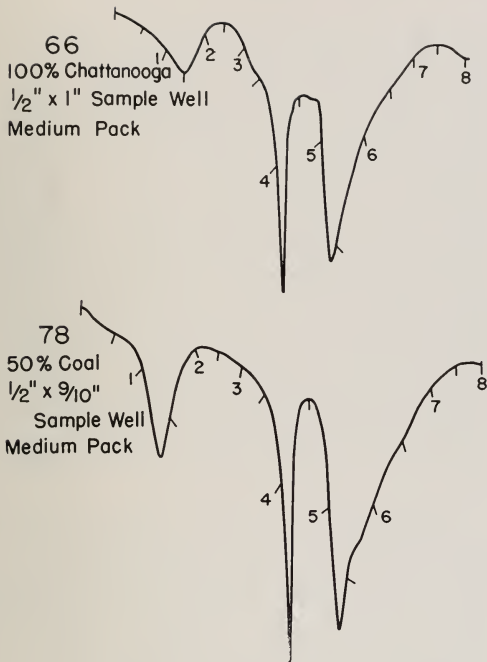


FIG. 3.—Thermograms showing the similarity of deflections obtained from coal and from bituminous shale.

ing or decreasing the effects of the particular factor involved. In the case illustrated in figure 7, a little less than 56.25 percent coal in the sample always produced an uninterrupted endotherm; slightly more than 56.25 percent coal always resulted in an interrupted one. If the balance is obtained by packing, looser packing inhibits and tighter packing enhances interruption. If heating rate is the controlling factor, an increase tends towards and a decrease tends away from interruption. If geometry of the specimen well is involved, a sufficiently shallow well eliminates and a sufficiently deep well produces the interruption. Whatever the factor, when conditions are imposed that tend to delay or temporarily stop free escape of decomposition gases from the sample as they form, the result is reflected on the thermogram, first by increased peak height and then by interruption of the main volatiles endotherm. In each case, the interval can be widened by continued increase of the influencing factor.

Careful consideration was given to the possibility that exothermic reaction might be responsible for the interruption interval,

but there is no supporting evidence for such an interpretation. The interval can not be explained by burning of gas within the sample well because the very conditions that should enhance burning—looser packing, shallower sample wells, or even uncovered samples—are those that inhibit interruption of the endotherm. When the furnace is opened immediately following upsweep from the point of interruption, the space outside the specimen wells is filled with gas in contact with the heating elements of the furnace. If burning does not take place here, where the gas is mixed with comparatively free air and where it is in contact with the hot kanthal wires, it is not likely to occur inside the sample well where the air supply is much more limited and temperature is several degrees lower.

Neither can the interruption be attributed to a difference in the content of the coal. In the instance demonstrated by curves 173 and 174 (fig. 7), where the same sample and experimental factors were involved, it is difficult to conceive that any substance might be present in one assay in quantity sufficient to produce such a large upward deflection and not be present in the next assay in quantity at least sufficient to produce some incipient deflection.

Hydrogenation also is ruled out as an explanation of the interruption interval because the temperature is still too low for breakdown of hydrocarbons and release of free hydrogen in significant quantities. Nor does it seem likely that any exothermic reaction could be made to vary to such extremes of time and temperature range as are reflected by the interruption interval. The shape of the re-entrant and the fact that its upward extent is always delimited to about the same relative position on the thermogram do not conform to the normal trends of exotherms.

The reversal of rise in furnace temperature cannot be related to exothermic reaction. Instead, it offers strong argument against an exothermic interpretation. The manner in which the thermogram responds to manipulation of factors that control gas escape supports the conclusion that it is not an expression of exothermic reaction.

DIFFERENTIAL THERMOGRAM TYPES

Figure 4 shows the wide variety of thermograms obtained from the same coal by manipulating experimental factors. The curve type varies progressively from a comparatively simple one (curve 37), through curves 185, 183, and 55 to those with interrupted endotherms, and then becomes increasingly complex through curves 82, 79, 43, 50, 93, 90, and 100.

The most noticeable change is the increasing size and height of the main volatiles endotherm until the interruption interval develops, after which the increasingly wider interruption interval becomes most noticeable. As the interruption interval increases in range, the temperature of the point of return rises progressively from 490° C. (curve 82) to about 860° C. (curve 100), but peak height of the point of return tends to decrease. The point of interruption also occurs at generally lower temperature, dropping rather gradually from about 455° C. (curve 82) to about 385° C. (curve 100). Here, too, gradual lessening of peak height is apparent.

Minor deflections on each of these first eleven thermograms can be followed through only part of the series. As the shape of the main volatiles endotherm alters, the smaller deflections either do not develop or are masked by larger ones. Correlation of these smaller deflections, especially those in the interruption interval, cannot be made with certainty from curve to curve. Variation in the nature of chemical and physical alteration of the sample is probable as heating conditions are progressively altered, but the exact nature of these changes is unknown and beyond the scope of this report.

The eleven thermograms discussed above are from tests made with an inconel specimen holder with wells $\frac{1}{2}$ inch in diameter and up to 1 inch deep. The sample was covered in each case. Experimental factors included progressively increasing the quantity of coal in relation to diluent, using an increasingly deeper specimen well, and packing the sample increasingly tighter. One or more of these factors was manipulated

to inhibit or interrupt escape of decomposition gases by introducing conditions favorable for congesting the interstitial particle space with tars and condensed tar vapors, and by imposing increased resistance to the swelling of the coal.

Thermogram 210 differs most noticeably from thermograms 90 and 100 in that the point of return develops as a rounded, rather than pointed, deflection. Maximum downward extent is reached between 950° and 1000° C. A heavier and closer-fitting cover was used in this test, and it was observed that the plastic coal had sealed this lid to the top of the sample holder so that no sudden exit of gas was permitted at higher temperature.

A nickel specimen holder with the same outside diameter as the inconel holder but with wells $\frac{3}{10}$ of an inch in diameter and $\frac{6}{10}$ of an inch deep was used for thermogram 126. The depth-to-diameter ratio of sample wells used for Nos. 126 and 43 are 10 to 5 and 9 to 5, respectively. The samples were diluted to 50 percent and medium-packed. Although deeper and narrower wells normally tend to produce more complex thermograms, curve 126 is less complex than 143.

Thermogram 104 was made with a nickel sample holder having wells $\frac{1}{4}$ of an inch in diameter and $\frac{6}{10}$ of an inch deep, a still greater depth in relation to diameter. Its moisture endotherm is sharper and narrower than that of 126, but the main volatiles endotherm is less prominent. Considering the smaller-diameter wells and the tighter packing used for curve 104, a still more complex thermogram type might have been expected.

The failure of thermogram types to follow the trend toward greater complexity when the nickel specimen holders were used probably was the result of two factors. First, the thermal conductivity of nickel is about four times that of inconel. Second, a relatively greater mass of metal and a smaller quantity of sample were involved when the nickel holders were used.

Webb (1954) pointed out that endothermic reaction commences in the hotter peripheral zones of the sample well. Rapid

flow of furnace heat into this superficial layer of coal from the mass of surrounding highly conductive metal masks the early part of the reaction by neutralizing the first endothermic cooling before it can affect the differential thermocouple. Deflection on the curve is thereby delayed until endothermic cooling reaches a value at which the heat from the surrounding metal can no longer penetrate the low conductive sample fast enough to neutralize it, whereupon the reaction manifests itself on the thermogram.

The principle applies when either inconel or nickel specimen holders are used, but is more pronounced with the nickel. The com-

paratively larger mass of more highly conductive metal and smaller-diameter specimen wells of the nickel sample holders enhance the neutralizing effect. The quantity of heat absorbed by endothermic cooling is smaller because of the smaller quantity of material required to fill the smaller wells. With the smaller-diameter wells of the nickel holder, furnace heat travels a proportionately greater part of the distance inward to the thermocouples through highly conductive metal and a proportionately shorter distance through the low-conductive sample. Sealing of interstitial particle space and temporary stoppage of gas escape may take

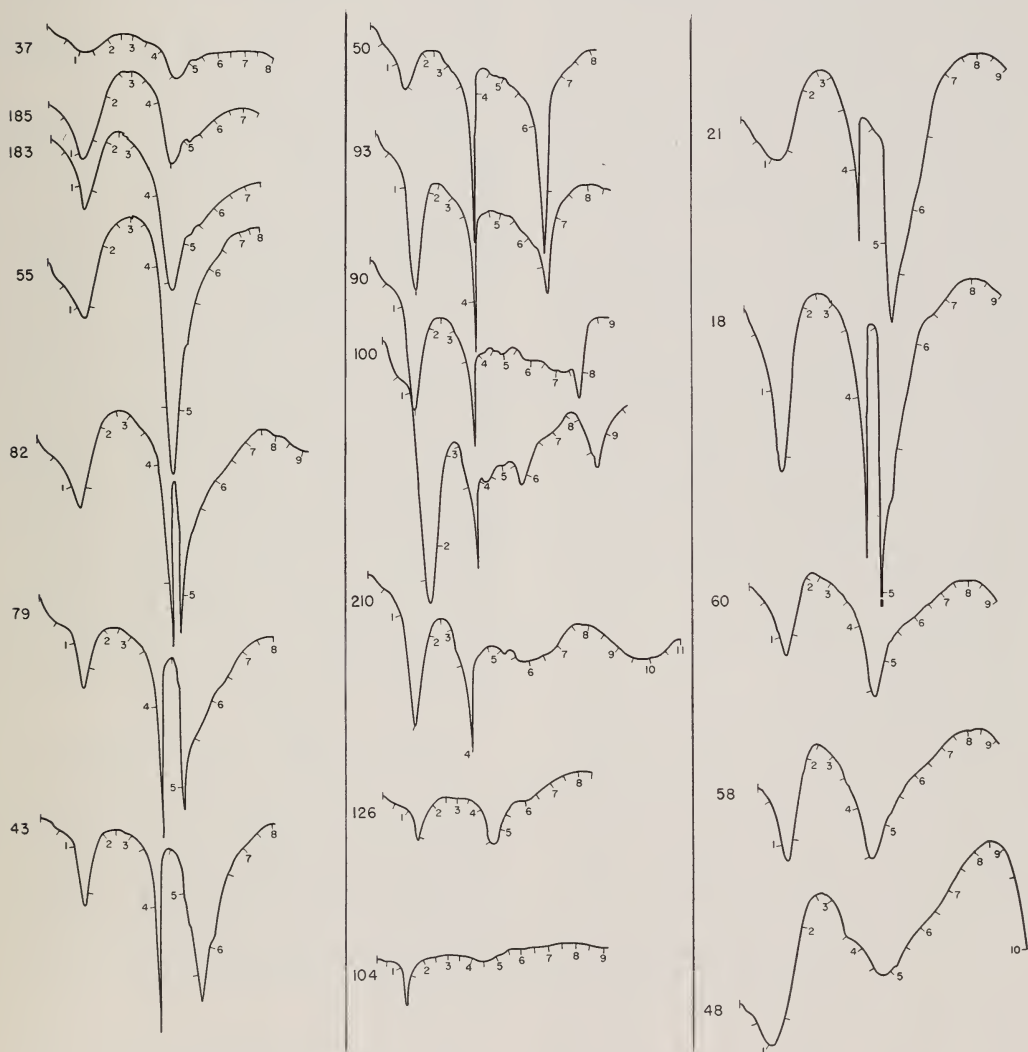


FIG. 4.—Thermogram types obtainable from one coal by manipulating experimental factors.

place more readily than in the 1/2-inch diameter well of the inconel specimen holder, but the blanketing influence of surrounding furnace heat maintains a closer thermal balance between the differential thermocouples and thereby tends to reduce the deflection on the thermogram.

Heating rate increased when the nickel holders were used, even though the same furnace-control settings were used as for the inconel. This increase is attributed to the difference in conductivity of the two metals and to the greater proportion of the distance that furnace heat travels through metal when smaller-diameter wells are used.

Additional tests were made with the two nickel specimen holders but the results were generally unsatisfactory, and nickel was abandoned in favor of inconel. No tests were made with nickel holders having well diameters of 1/2 inch, or with a smaller mass of metal, hence these results do not imply that nickel is an unsatisfactory material to use for sample holders.

The right-hand row of thermograms of figure 4 are of tests made with the inconel holder with no cover over the specimen. Because of its wider interruption interval, curve 21 is considered more complex than curve 18. Actually, however, the sample for curve 21 was medium-packed while that for curve 18 was tightly packed, and the sample-well dimensions were the same in both cases. Although the two curves appear contrary to the expected trend, they were selected to emphasize the difficulty of controlling uncovered samples.

Thermograms 60, 58, and 48 are of bright clarain heated in a sample well 1/2 inch in diameter and 9/10 of an inch deep. The influencing factor probably was packing, which was tight for curve 60, medium for curve 58, and loose for curve 48. Progressively increasing exothermic tendency is apparent as the degree of packing is diminished. The increase of exothermic trend before the start of the main volatiles endotherm is believed to be due to oxidation resulting from the entrance of air into the greater interstitial particle space allowed by looser packing. Above 460° C., and after volatiles evolution has passed its maximum,

the temperature is high enough for burning. The rate of burning increases as the degree of packing is diminished and is reflected by the increasingly pronounced exothermic trend above the main volatiles endotherm. At the end of the test of curve 48, only a powdered ash residue was left in the specimen well.

These five thermograms show that burning to completion can be prevented, even when no cover is used, if the sample well is deep enough or if the sample is tightly packed. Burning commences at the top of the specimen and proceeds downward. If conditions are present to retard its progress it does not extend down to the differential thermocouple, but heat of oxidation no doubt affects the differential thermocouple even though actual burning is above it.

In general, it was observed that with the specimen uncovered experimental factors exerted less influence and, except where conditions were such that complete burning could take place freely, accurate reproduction of thermograms was almost impossible.

Figure 5 summarizes the effects exerted by variation of sample-well dimensions, degree of packing, leaving a 1/4-inch cushion of air between the top of the specimen and the cover, and heating with no cover. All samples consisted of bright clarain diluted with 50 percent alundum. Table 1 gives other experimental data involved. Each thermogram is considered as the most representative type occurring under the particular experimental conditions. Progressive development of curve type results as any one factor is increased or decreased while all others are kept constant.

IMPORTANCE OF SAMPLING

The necessity for careful sampling in making accurate analyses cannot be overemphasized. The chemical and physical differences of individual ingredients of banded bituminous coal have long been recognized, and the importance of selecting representative samples is fully appreciated by all who work with coal.

All curves shown in figures 4 and 5, and discussed in the preceding pages, were made

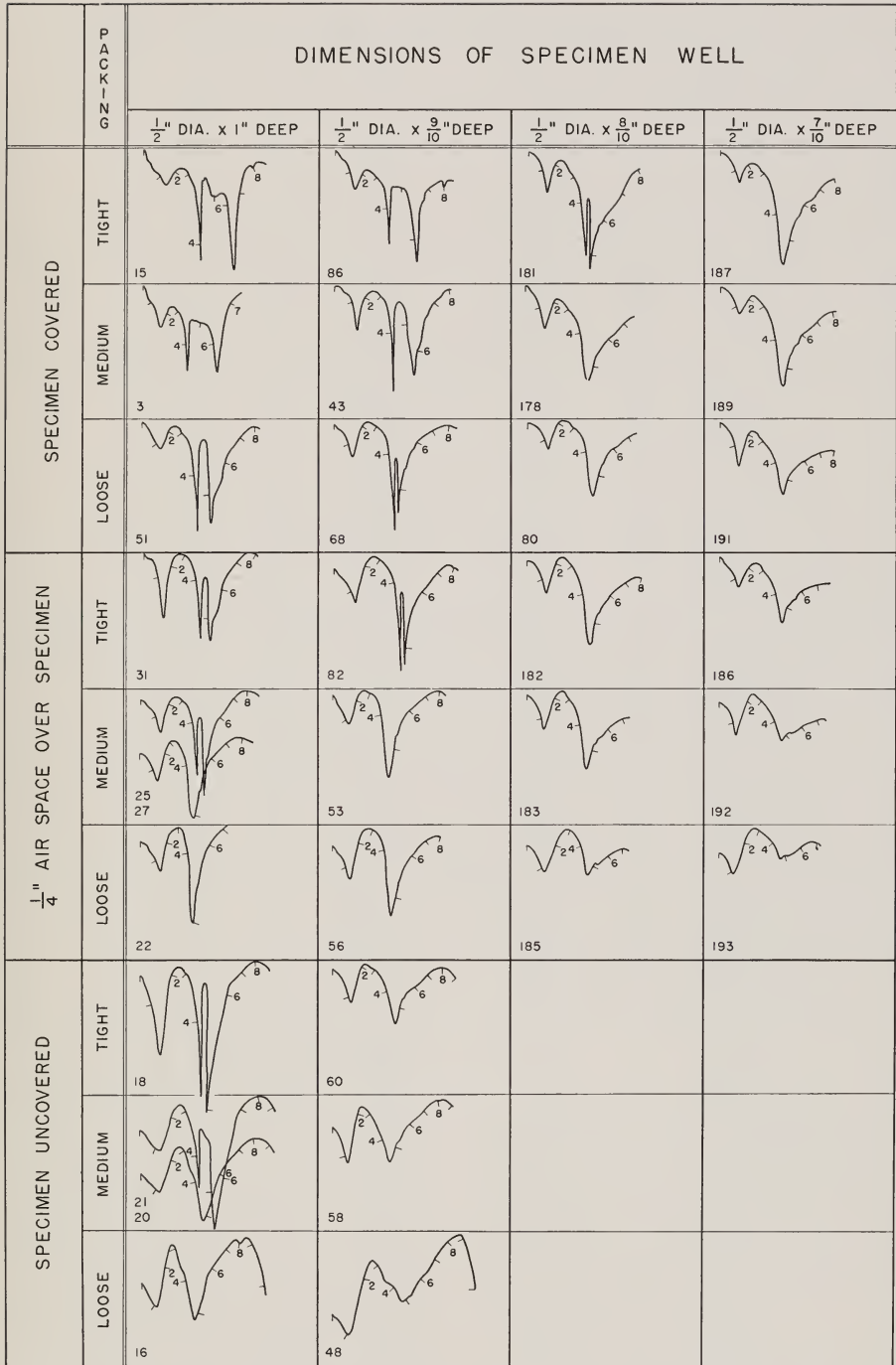


FIG. 5.—Summary of thermogram types showing the control exerted by the degree of packing, by geometry of the specimen holder, and by covering the sample.

TABLE 1.—SUMMARY OF THE VARIOUS EXPERIMENTAL FACTORS APPLIED TO EACH ANALYSIS

Curve	Sample well* Diam.—depth	Cover**	% Coal	Pack***	Remarks
3	1/2-1	Yes	50	M	
15	1/2-1	Yes	50	T	
16	1/2-1	No	50	L	
18	1/2-1	No	50	T	
20	1/2-1	No	50	M	
21	1/2-1	No	50	M	
22	1/2-1	Yes C	50	L	
25	1/2-1	Yes C	50	M	
27	1/2-1	Yes C	50	M	
31	1/2-1	Yes C	50	T	
37	1/2-9/10	Yes	6.25	T	
43	1/2-9/10	Yes	50	M	
48	1/2-9/10	No	50	L	
50	1/2-9/10	Yes	50	T	
51	1/2-1	Yes	50	L	
53	1/2-9/10	Yes	50	M	
55	1/2-9/10	Yes C	50	L	
56	1/2-9/10	Yes C	50	L	
58	1/2-9/10	No	50	M	
60	1/2-9/10	No	50	T	
66	1/2-1	Yes		M	100% Chattanooga shale
67	1/2-9/10	Yes	50	L	
68	1/2-9/10	Yes	50	L	
78	1/2-9/10	Yes	50	M	
79	1/2-8/10	Yes	50	T	
80	1/2-8/10	Yes	50	L	
82	1/2-9/10	Yes C	50	T	
86	1/2-9/10	Yes	50	T	
89	1/2-9/10	Yes	75	T	
90	1/2-9/10	Yes	75	T	
92	1/2-9/10	Yes	37.50	T	
93	1/2-9/10	Yes	67.50	T	
94	1/2-9/10	Yes	87.50	T	
96	1/2-9/10	Yes	25	T	
97	1/2-9/10	Yes	27.50	T	
98	1/2-9/10	Yes	31.25	T	
99	1/2-9/10	Yes	12.50	T	
100	1/2-9/10	Yes	100	T	
104	1/4-6/10	Yes	50	T	Nickel specimen holder Nickel specimen holder
126	3/10-6/10	Yes	50	M	
143	1/2-9/10	Yes	50	L	10-11° C. per min. 15-18° C. per min. 22-26° C. per min. 27-31° C. per min. 12-13° C. per min.
145	1/2-9/10	Yes	50	L	
147	1/2-9/10	Yes	50	L	
148	1/2-9/10	Yes	50	L	
149	1/2-9/10	Yes	50	L	
150	1/2-9/10	Yes	50	L	11-12° C. per min. 15-17° C. per min. 7° C. per min.
153	1/2-9/10	Yes	50	L	
154	1/2-9/10	Yes	50	L	
158	1/2-9/10	Yes	50	L	
159	1/2-9/10	Yes	50	L	
160	1/2-9/10	Yes	50	L	
161	1/2-9/10	Yes	50	L	
162	1/2-9/10	Yes	50	L	
163	1/2-9/10	Yes	50	L	
164	1/2-9/10	Yes	25	L	

TABLE 1.—(Concluded)

Curve	Sample well* Diam.—depth	Cover**	% Coal	Pack***	Remarks
169	1/2-9/10	Yes	87.50	L	
172	1/2-9/10	Yes	50	L	
173	1/2-9/10	Yes	56.25	L	
174	1/2-9/10	Yes	56.25	L	
175	1/2-9/10	Yes	100	L	
176	1/2-9/10	Yes	75	L	
177	1/2-9/10	Yes	31.25	L	
178	1/2-8/10	Yes	50	M	
181	1/2-8/10	Yes	50	T	
182	1/2-8/10	Yes C	50	T	
183	1/2-8/10	Yes C	50	M	
185	1/2-8/10	Yes C	50	M	
186	1/2-8/10	Yes C	50	T	
187	1/2-7/10	Yes	50	T	
189	1/2-7/10	Yes	50	M	
191	1/2-7/10	Yes	50	L	
192	1/2-7/10	Yes C	50	M	
193	1/2-7/10	Yes C	50	L	
194	1/2-9/10	Yes	100	L	Selected vitrinite
195	1/2-9/10	Yes	100	L	Selected dull attritus
196	1/2-9/10	Yes	100	L	Selected fusinite
198	1/2-9/10	Yes	66.66	L	— 28 mesh
199	1/2-9/10	Yes	66.66	L	—270 mesh
200	1/2-9/10	Yes	66.66	L	—100 mesh
201	1/2-9/10	Yes	66.66	L	—270 mesh
202	1/2-9/10	Yes	66.66	L	— 65 mesh
203	1/2-9/10	Yes	66.66	L	—200 mesh
204	1/2-9/10	Yes	66.66	L	—200 mesh
205	1/2-9/10	Yes	66.66	L	
206	1/2-9/10	Yes	66.66	L	0 ohms resistance
207	1/2-9/10	Yes	66.66	L	100 ohms resistance
208	1/2-9/10	Yes	66.66	L	150 ohms resistance
209	1/2-9/10	Yes	66.66	L	300 ohms resistance
210	1/2-9/10	Yes	66.66	L	Heavy cover

*Measurements in fractions of one inch.

***"C" indicates ¼-inch air cushion between specimen and cover.

****"L", "M", "T"—loose, medium, or tight packing.

with random samples of bright-banded clarain from the same coal core. Consideration must therefore be given to the influence of sample variability resulting from the heterogeneity of banded coal. The influence is minimized somewhat in this case by the fact that, even though sampling was random, it was restricted to narrow-banded bright clarain. By that restriction, curve variation was limited sufficiently for the various experimental factors to exert a dominating influence.

The results of tests made to show how sample variability affects differential thermograms are given in figure 6. All these

thermograms were made with the inconel sample holder. The wells were ½ inch in diameter and 9/10 of an inch deep. Samples were loosely packed and covered. Each of these factors lends itself to good thermogram reproducibility so that curve variety can be attributed almost wholly to differences in the samples.

The four thermograms in the right-hand row of figure 6 were made with undiluted samples. Banded ingredients were selected with as much care as possible. The bright clarain (curve 175) consisted of about 50 percent vitrinite, by visual estimation, and was typical of the bright clarain that con-

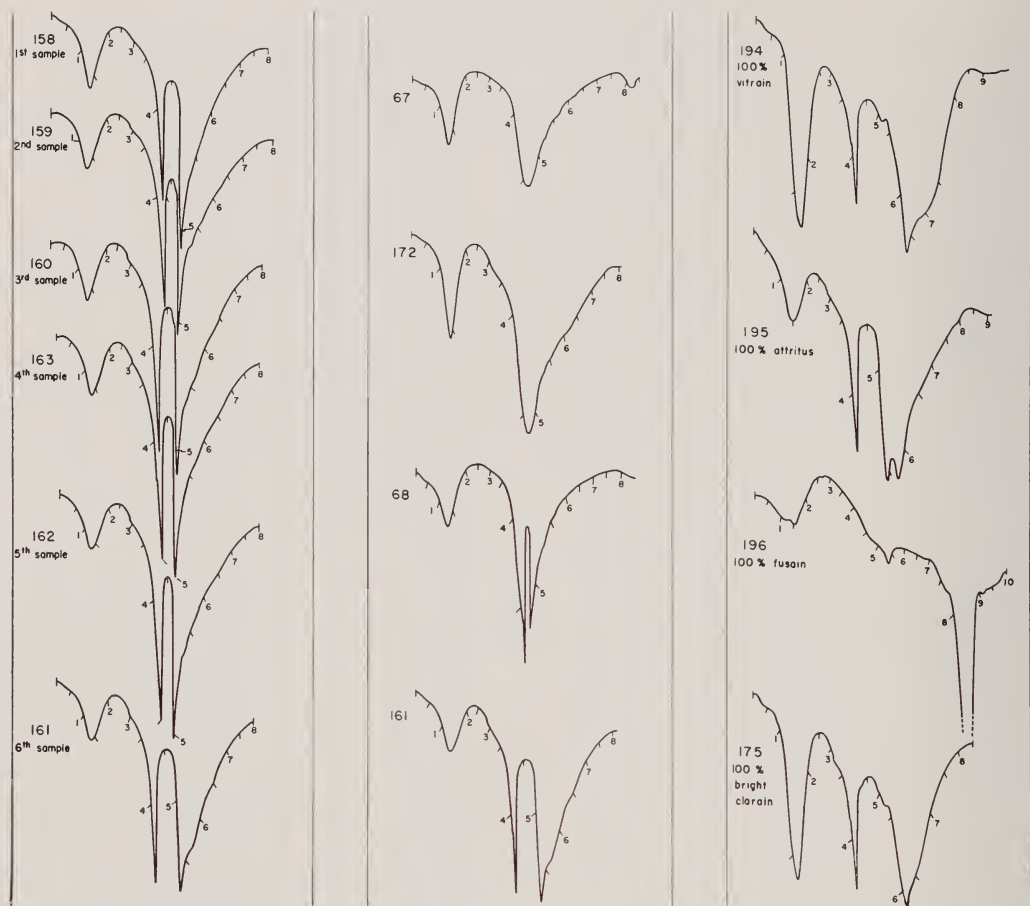


FIG. 6.—Thermograms showing variations resulting from heterogeneity of banded coal.

stitutes 51.1 percent of the coal core. Dull attritus containing an estimated 20 percent vitrinite was used for curve 195. The fusain sample (curve 196) was badly contaminated with mineral matter.

Similarity of curves 194 and 175, vitrain and bright clarain containing 50 percent vitrinite, indicates that in this coal the vitrinite content of bright clarain exerts considerable influence during thermal analysis. Such similarity of curves might not occur, however, in a coal having clarain of a duller variety. Well-fused coke buttons developed from both the bright clarain and the vitrain, but that of the vitrain was considerably harder.

A powdered and completely unfused residue was left in the specimen well after the dull attritus was heated. Interruption of

the main volatiles endotherm indicates formation of sufficient tar to cause temporary interruption of gas escape from the sample. The comparatively narrower interruption interval shows that less gas pressure was necessary to overcome the interruption than was required in the vitrain and clarain samples.

Thermograms 67, 172, 68, and 161 of hand-picked bright clarain were selected at random from the files to show the maximum variation of curve types that can result from samples that *appear* to be alike. In each case the sample consisted of equal parts by volume of coal and alundum. The variation is of sufficient magnitude to show that random sampling, even when restricted to bright clarain, is not satisfactory for precise quantitative or qualitative work.

The series of thermograms in the left-hand row of figure 6 are of a test designed to check a possible variable resulting from the final grinding of a sample preparatory to analysis. It was suspected that if a quantity of coal was ground and sieved only until enough minus 100 mesh was obtained for the analysis, the plus 100 mesh remaining on the screen might not have the same composition as that which had crushed more readily. Therefore, enough 10 by 28 mesh bright clarain was prepared to make six analyses. The entire amount was then put into the mortar and ground until enough minus 100 mesh was obtained for the first run. This sample was set aside and the grinding continued until enough minus 100 mesh was obtained for the second test. The process was continued until six samples of minus 100 mesh size had been prepared. The sample for the sixth consisted of the last material, supposedly the most resistant, to pass through the minus 100 mesh sieve.

Comparison of the thermograms indicates that, with the possible exception of the sixth sample (curve 161), which has a somewhat broader interruption interval, no great difference existed in the individual samples. The variability of the first five curves is well within the limits of accuracy of methods and equipment used.

It is nevertheless recommended that when a sample is to be crushed, the entire quantity be ground to the desired size and enough to fill the sample well be taken from the whole. If undiluted samples had been used, a greater difference might have resulted.

EFFECTS OF DILUTING THE SPECIMEN

Diluted samples were used in most cases because of difficulty encountered in removing the fused residue of undiluted coal without damaging the thermocouple. The effects of varying amounts of an inert diluent were checked under both loose and tight packing conditions (fig. 7). A specimen well $\frac{1}{2}$ inch in diameter and $\frac{9}{10}$ of an inch deep with a cover over the sample was used. A bulk sample of 10 by 28 mesh

bright clarain, from which amounts were taken and prepared for individual analyses, was used for all the loosely packed runs. The same method of sampling was used for the tightly packed tests. Thus, uniform samples were used for all curves under each condition of analysis, but the same bulk sample was not used for both the loosely packed and tightly packed analyses.

A well-developed series of curve types resulted with tightly packed samples. The series is equally well developed with loose packing but is not as complete, the maximum temperature of the point of return being about 610° C. as compared to 860° C. with tight packing.

Diluting may be advantageous for reasons other than ease of removing the residue. When the height and steepness of the main volatiles endotherm are reduced, smaller deflections that tend to be masked by long, sweeping curves may appear to better advantage. On the whole, more accurate reproduction was possible when samples were diluted and loosely packed. A loosely packed specimen of not more than 50 percent coal appeared to give the best reproducibility with the methods and equipment used in this study. There are indications, however, that tight packing produces thermograms with greater detail and on which individual deflections can better be differentiated from each other.

If alundum is used as the reference material, diluting the coal with the same material serves to lessen the differences of heat capacity, heat transfer, and heat conductivity and diffusivity that exist between coal and alundum. However, a diluent and comparison medium having particle size and thermal characteristics more like those of coal would be more desirable.

The influence of an inert diluent upon coal thermograms shows that accurate quantitative work by differential thermal analysis could be limited by the presence of shale in the sample, even though the impurity contained no reactive minerals. This factor must be considered if quantitative determination of volatile content of coal is attempted.

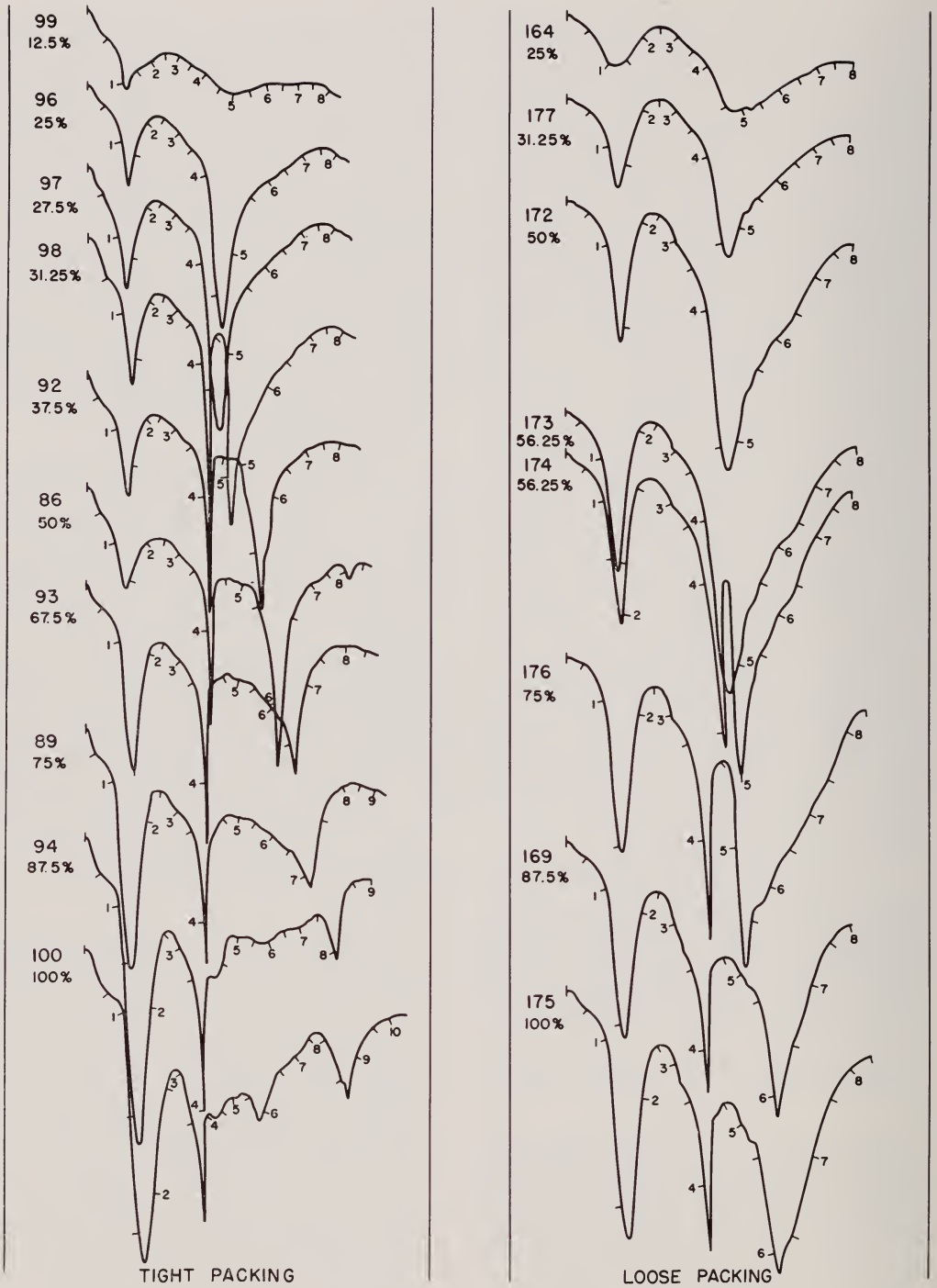


FIG. 7.—Thermograms showing the effects of diluting the specimen with alundum. Percentage figures refer to the quantity of coal in relation to diluent.

EFFECTS OF PARTICLE SIZE

Considerable variation of thermograms was obtained with samples of different maximum particle size (fig. 8). All analyses for checking this factor were made with the inconel sample holder with specimen wells $\frac{1}{2}$ inch in diameter and $\frac{9}{10}$ of an inch deep. Samples were loosely packed and covered. A bulk sample of 10 by 28 mesh bright clarain was prepared from which individual samples were taken and prepared for each test.

No attempt was made to adopt a lower size limit for individual samples because it was felt that uniform samples for all analyses could not be assured if part of the sample was discarded each time. Frequent sieving during the final grinding was more closely adhered to than normally, however, so that the quantity of very fine sizes would be held as close to a minimum as possible. The exact particle size of the alundum diluent was not determined, but it was at least small enough to pass through a 270 mesh Tyler sieve. Two parts of coal to one of diluent were used to reduce the effect of the fine-size alundum.

A gradual diminution of the interruption interval occurs as maximum grain size decreases from minus 28 to minus 200 mesh. In a minus 28 mesh sample there necessarily must be a considerable range of particle size in spite of frequent sieving. This size range is progressively shortened, however, as maximum particle size is reduced through minus 65, 100, and 200 mesh. When minus 200 mesh or smaller is used, any effect of particle size appears to be negligible as far as its reflection on the thermogram is concerned. Compare curve 204 (minus 200 mesh) with curve 199 (minus 270 mesh), and curve 203 (minus 200 mesh) with curve 201 (minus 270 mesh). Then compare the similarity of curves 204 and 201 (minus 200 and 270 mesh, respectively) and of curves 203 and 199 (also minus 200 and 270 mesh, respectively). The four are sufficiently alike to be considered within limits of experimental accuracy, regardless of particle size.

Bulk density decreases with decreasing

particle size and admits a smaller quantity of sample into a given space volume. It also seems likely that narrower size range would afford better permeability to passage of gases since greater total surface area of particles would give more frictional resistance to settling in the specimen well. It has been suggested that coal particles of .17 mm. or smaller behave as spheres (Staeckel and Radt, 1934).

The progressively smaller interruption interval produced by samples of smaller maximum particle size shows that resistance to expansion and escape of gas decreased with decreasing particle size until the maximum size was as small as minus 200 mesh.

Direct experiments carried out with coking coals have shown that the formation of coke could be prevented entirely if the coal particles were very small (Sweitoslawski, 1942, p. 115). The condition of the residue from these tests confirms these findings. Hard and well-fused coke buttons were found after minus 28 and minus 65 mesh samples were heated, and a weaker button after a minus 100 mesh size was heated. Only unconsolidated powder was left after minus 200 and 270 mesh sizes were heated. Renewal of gas escape following temporary interruption appears to have occurred with development of sufficient pressure to bind the coal particles.

The tests demonstrate the necessity of following uniform practices of sizing during sample preparation. Sizing is imperative for elimination of the uncontrollable variable introduced by random crushing of the sample. Minus 200 or smaller mesh size seems to settle uniformly into the specimen well and thereby helps to solve the difficult problem of uniform packing. It is not suggested, however, that this is the final answer to the problem. More study of particle size and of crushing methods is needed.

EFFECTS OF HEATING RATE

To study the effects of heating rates, a series of tests was made in which all other experimental factors were held constant. Samples for each analysis were taken as re-

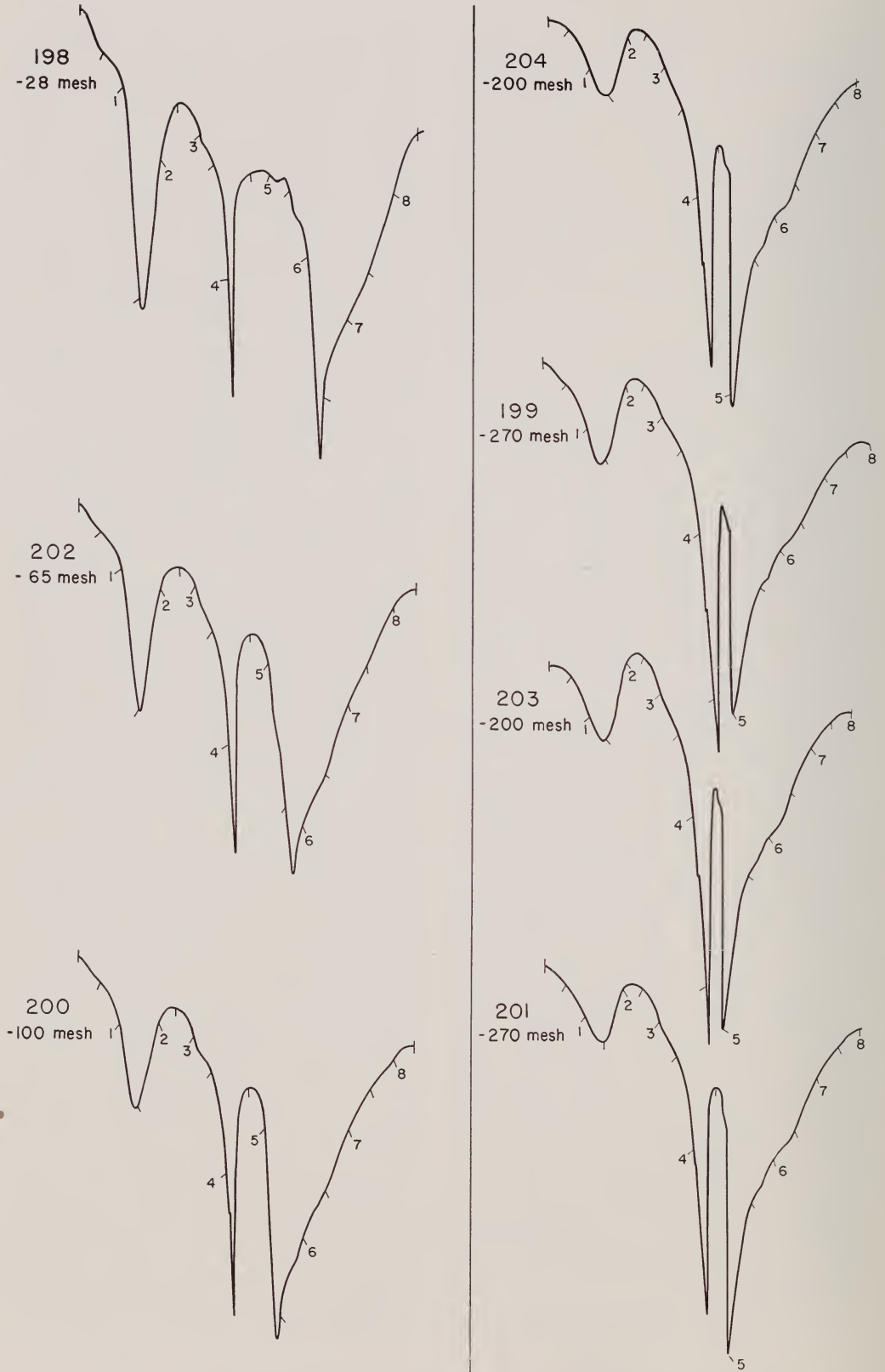


FIG. 8.—Thermograms showing the influence of coal particle size.

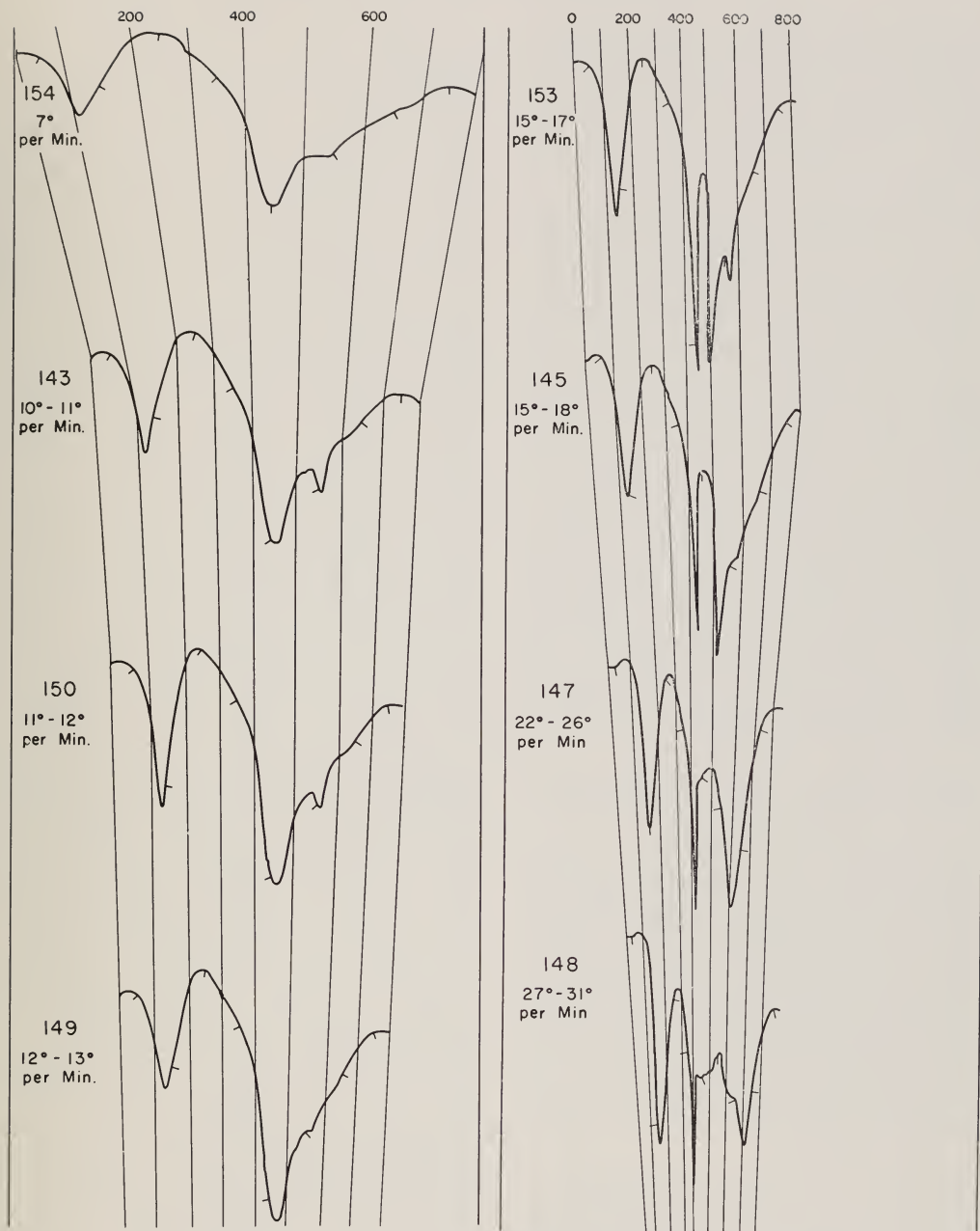


FIG. 9.—Thermograms showing progressive alteration with increased heating rate.

quired from a bulk sample of 10 by 28 mesh bright clarain to insure uniform samples for all thermograms of the series. Each sample was crushed to desired size, diluted to equal portions of coal and alundum, loosely packed, and covered. The sample well was $\frac{1}{2}$ inch in diameter and $\frac{9}{10}$ of an inch deep.

Gradual development of curve type from simple to complex is apparent as heating rate is increased (fig. 9). Increasing peak height of the main volatiles endotherm is followed by interruption and then by gradual widening of the interruption interval.

The rate of temperature rise was not exactly linear throughout the range of any one

thermogram, as shown by the lines connecting each 100° C. mark. A small endothermic deflection at about 550° C. is more or less pronounced on most of the thermograms. No attempt was made to interpret its cause.

This series again demonstrates the influence upon the thermogram if evolved gases are not permitted to escape from the specimen as they form. During slow heating, volatile matter escapes without interruption, but as the heating rate is increased the sample well becomes congested with tar vapors and the sealing of interstitial particle space results. At a rate of 15° to 17° C. per minute (curve 153), the congested condition inside the sample well is reflected by the development of an interruption interval that grows increasingly wider as heating rates are increased. Further investigation of heating rate is needed. The decomposition process of coal is such that a slower rate might permit certain reactions to more nearly reach completion and thus separate them on the thermogram.

EFFECTS OF GALVANOMETER RESISTANCE

The thermograms of figure 10 are included to show how one undesirable feature, the long, sweeping endotherm characteristic of coal analyzed under the conditions tested in this study, can be reduced. Inhibiting the downsweep of endotherms by greater resistance in series with the galvanometer allows minor deflections, otherwise partially or completely masked, to be shown to better advantage.

Uniform samples were used in each test, diluted 50 percent with alundum, and loosely packed in a sample well 1/2 inch in diameter and 9/10 of an inch deep. A metal cover was used over the samples.

It sometimes may be desirable to run a sample at several different resistances so that deflections masked under one condition can be brought out under another.

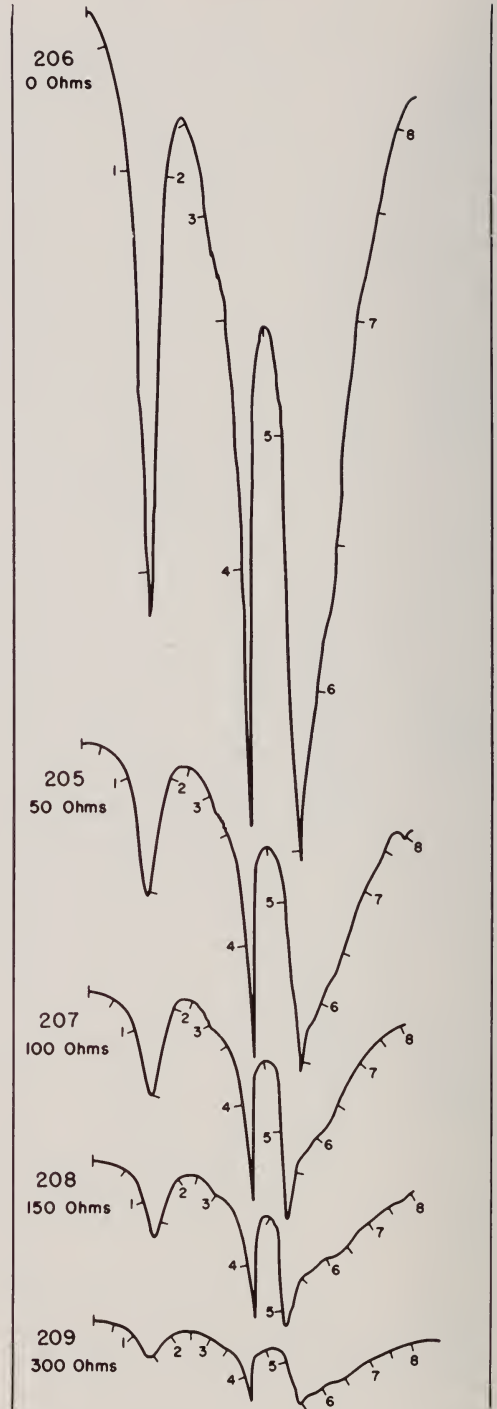


FIG. 10.—Thermograms showing the influence of differences in galvanometer resistance.

SUMMARY AND CONCLUSIONS

In general it may be said that, insofar as the inherent differences of coal and clay permit a comparison of experimental factors, and insofar as the experiments conducted can be compared with those of Arens (1951), thermograms respond in the same general direction whether they are of clay or of coal. The magnitude of the response, however, seems to be greater in coal.

It should be borne in mind that variations are orderly and explainable and respond moderately well to control. Proper control over experimental factors eventually may lead to the development of a thermogram type with a maximum amount of interpretable detail. The wide variety of curves obtained in this study, and by other workers who have made differential thermal studies of coals with different equipment and under other conditions, shows that under some circumstances many deflections are partially or completely masked. In many cases, experimental factors rather than the coal itself are responsible.

Solving the many problems involved in differential thermal studies of coal was not the primary object of this investigation. Some of the problems have been pointed out and emphasized, and an approach to the solution of a few of them suggested. Design of the specimen holder and control over oxidation are among the major items requiring modification.

The problem of heat transfer through the specimen holder can be solved by using separated holders for the reference material and the sample. Sample holders with thin walls might reduce the smothering effect of an excessive mass of hot metal around the specimen. Further study of design, mass, geometry, and composition of the holder is needed.

Formation of ash on the surface of the specimen indicates oxidation, but the extent

of its effect cannot be determined. Air also enters through the small thermocouple opening in the side of the specimen well, and comes into contact with the sample right at the differential thermocouple where very slight oxidation conceivably could exert a very strong and uncontrollable influence. Oxidation might best be eliminated by an atmosphere of inert gas.

As mentioned in the discussion of diluents, the alundum used in these tests is not considered the most desirable comparison material or diluent for coal analysis. A material having thermal characteristics more like those of coal and that can be crushed to particle size more nearly equal to that of coal would be more suitable.

The differential thermal technique appears to offer possibilities as an additional tool for qualitative coal study, particularly when used with data obtained from other types of investigation. However, any evaluation of differential thermal data or any interpretation of thermograms must be made with full cognizance of the limits of accuracy of the method and equipment employed. There is need for further experimentation before full evaluation of this technique can be determined. Its ultimate value probably will depend upon the degree to which differences in coals can be made to register on the thermogram as individual entities that can be differentiated one from the other. There is no longer any doubt that coals of different ranks and types do yield different thermograms. The need is for refinement of the technique so that as many as possible of the minor variations in coals can be detected by the deflections they produce.

Since minor variations of experimental factors and equipment design do cause such diversity of curve types, it is suggested that reports of coal study by differential thermal analysis contain detailed descriptions of equipment and methods employed.

REFERENCES

- ARENS, P. L., 1951, A study of the differential thermal analysis of clays and clay minerals: The Hague, Excelsiors Foto-Offset, 131 p.
- BREGER, I. A., 1950, The chemical and structural relationship of lignin to humic substances: Conference on the Origin and Constitution of Coal, Nova Scotia Dept. Mines, Nova Scotia Research Foundation, p. 111-116.
- GLASS, H. D., 1954, Investigation of rank in coal by differential thermal analysis: *Econ. Geol.*, v. 49, no. 3, p. 294-310.
- GRIM, R. E., and ROWLAND, R. A., 1942, Differential thermal analysis of clay minerals and other hydrous materials: *Am. Mineralogist*, v. 27, no. 11, p. 746-761; no. 12, p. 801-818.
- HOLLINGS, H., and COBB, J. W., 1923, A thermal study of the carbonization process: *Fuel*, v. 2, no. 10, p. 322-333.
- National Research Council, 1945, Chemistry of coal utilization, v. 1: New York, John Wiley, 920 p.
- STAECKEL, W., and RADT, W. P., 1934, Effect of grain size on the bulk density of coking coal: *Fuel*, v. 13, no. 9, p. 282-285; no. 10, p. 311-313.
- STOTT, J. B., and BAKER, O. J., 1953, Differential thermal analysis of coal: *Fuel*, v. 32, no. 4, p. 415-427.
- STUTZER, O., and NOE, A. C., 1940, Geology of coal: Chicago, Univ. Chicago Press, 428 p.
- SWEITOSLAWSKI, W., 1942, Coke formation process and physico-chemical properties of coals (Polish Inst. Series 1): New York, Polish Inst. of Arts and Sciences in America, 140 p.
- WEBB, T. L., 1954, Comparative performance of nickel and porous alumina sample holders for differential thermal analysis: *Nature*, v. 174, no. 4432, p. 686-689.
- WHITEHEAD, W. L., 1950, The vacuum differential analysis of coals: Conference on the Origin and Constitution of Coal, Nova Scotia Dept. Mines, Nova Scotia Research Foundation, p. 100-110.
- , and BREGER, I. A., 1950, Vacuum differential thermal analysis: *Science*, v. 111, no. 2881, p. 279-281.

